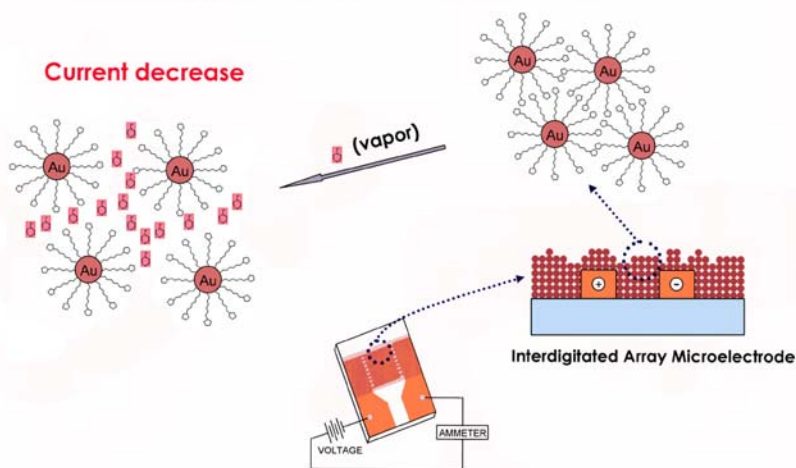


# Surface Science Studies of Oligothiophene Adsorption on Clean and Modified Aluminum Surfaces

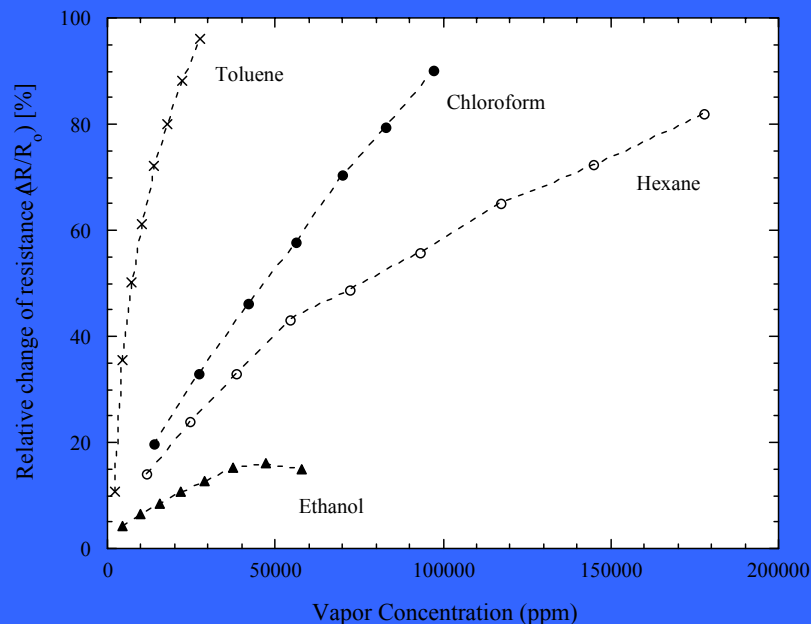
James E. Whitten, University of Massachusetts Lowell, **DMR-0089960**

- Thiophene-terminated alkanethiols have been synthesized, and their self-assembly on gold surfaces has been characterized. Aluminum has been deposited on the self-assembled monolayers to study the interaction of aluminum with thiophene.
- Thiophene-terminated alkanethiols have also been used to coat gold nanoparticles, and organic vapor sensors have been fabricated from the monolayer protected gold nanoparticle films.

## Mechanism of a Chemiresistor-Type Vapor Sensor



Change of Resistance vs Organic Vapor Concentration for Films Comprised of Gold Nanoparticles Protected by 12-(3-thienyl)dodecanethiol



The self-assembled monolayers of thiophene-terminated alkanethiols have been characterized by a variety of methods, including ellipsometry, contact angle measurements, and photoelectron spectroscopies. The details may be found in the following paper from our group: H. Ahn, et al., *Langmuir*, vol. 19, p. 5303 (2003).

Studies of the thermal deposition of aluminum on thiophene-terminated alkanethiol monolayers is significant because aluminum is commonly used as an electrode in organic electronic devices. Our group has investigated the deposition of aluminum on these types of monolayers, and the results are reported in: H. Ahn, et al. *J. Phys. Chem. B*, vol. 107, p. 6565 (2003).

These types of organic vapor sensors were first discovered by Hank Wohlten and Arthur Snow (at Naval Research Laboratory). However, the Whitten group is the first to study sensors made using thiophene-terminated alkanethiol protected gold nanoparticles. The films are spin-coated onto interdigitated microelectrode arrays (commercially available from Microsensor Systems).

Chemical selectivity could be achieved by using two or more films made from gold nanoparticles protected with alkanethiols having different terminal functional groups.

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## **Broad Impacts:**

- Polythiophenes comprise a major class of semiconducting organic materials.

Applications include organic light-emitting diodes, field-effect transistors, and photovoltaics. Thiophene-terminated self-assembled monolayers can serve as model systems to understand the chemistry of thiophene interfaces.

- Organic vapor sensors may be fabricated from monolayer-protected gold nanoparticle films. Sorption of organic vapors causes swelling of the film and changes in electrical resistance. These studies could have homeland security applications.

## **Education and Outreach:**

- Several Ph.D. and M.S. graduate students and undergraduate chemistry majors have participated in this research. These students have gained important experience in materials chemistry, surface science, and organic electronics.

- This research has also permitted the PI to forge collaborative relationships with various industrial and government laboratories, including Konarka Technologies (a company fabricating flexible organic photovoltaic devices) and the Naval Research Laboratory (which is interested in sensor applications).

The sorption of organic vapor causes the monolayer-protected gold nanoparticle films to swell. This leads to an increase in the distances between nearby gold nanoparticles and lower electrical conductivity. The conductivity, which is due to electron hopping, is strongly dependent on the separation between adjacent gold cores.

Generally, the higher the concentration of organic vapor, the more swelling there is in the film. This is correlated with solubility properties of the monolayer-protected gold particles, as we have shown in H. Ahn, et al., *Chemistry of Materials*, vol. 16, p. 3274 (2004).

For polar organic molecules, such as ethanol, a decrease in resistance (and an increase in conductivity of the films) occurs at high vapor concentration due to an increase in the dielectric constant of the medium between the gold cores.